ROTATIONAL SPECIFIC HEAT AND HALF QUANTUM NUMBERS

By Richard C. Tolman

Abstract

Application of half quantum numbers to the theory of the rotational specific heat of hydrogen.—It is shown from a consideration of infra-red rotation-oscillation spectra, that the lowest possible azimuthal quantum number for a non-oscillating rotating molecule of the rigid "dumb-bell" model can have only the values zero, one, or one-half. An elementary theory of quantization in space for the new case of half quantum numbers is then developed which shows that the a priori probabilities for successive levels of rotational energy stand in the ratios of 1, 2, 3, ... The specific heat curve for diatomic hydrogen to 300°K is then calculated on the basis of the energy levels and of a priori probabilities corresponding to half quantum numbers, and is compared with the experimental points and with the curves calculated by Reiche using zero and one as the lowest possible azimuthal quantum number. At low temperatures the new curve agrees with the experimental data as well as any curve of Reiche's. At the higher temperatures, none of the curves agree with all the experimental points. *The moment of inertia for the hydrogen molecule* corresponding to the new curve is $J=1.387\times10^{-41}$ gm cm^2, about two-thirds the values assumed by Reiche, 2.095 to 2.293×10^{-41}, and agrees better with the conclusion of Sommerfeld from the separation of lines in the many lined spectrum of hydrogen, that the moment of inertia of an excited hydrogen molecule is 1.9×10^{-41} gm cm^2, which should be greater than that of the unexcited molecules involved in specific heats. Hence the possibility of half quantum numbers seems worthy of consideration.

Introduction

IT IS the purpose of the following paper to investigate the possibility of accounting for the rotational specific heat of diatomic hydrogen by assuming for the hydrogen molecule the rigid "dumb-bell" model with two degrees of freedom, making use of the "first" form of the quantum theory, and taking the lowest possible azimuthal quantum number as one half instead of either zero or one as has previously been done.

We shall first show from a consideration of infra-red rotation-oscillation spectra, that the only possible values for the lowest azimuthal quantum number for the non-oscillating molecule are zero, one half, and one, and shall point out that the new assumption has the advantage of making the lowest azimuthal quantum number one half for both the oscillating and non-oscillating molecule, instead of different for the molecule in the two states. We shall then develop an elementary theory

of quantization in space for half quantum numbers and show that such a theory leads in a very simple and unconstrained manner to a priori probabilities for successive energy levels which stand in the ratios 1, 2, 3, 4 etc. Using the new a priori probabilities and new energy levels, the specific heat curve for hydrogen will then be calculated and compared with the experimental data of Eucken[1] and of Scheel and Heuse.[2] The results will also be compared with those calculated by Reiche[3] on the assumptions of zero and one as the lowest possible azimuthal quantum number, and various assumptions as to a priori probabilities.

The new specific heat curve thus obtained agrees with the experimental points at low temperatures as well as any curve of Reiche's, and has the advantage of giving a lower value for the moment of inertia of the hydrogen molecule, a result which is supported by the separation of the lines in the many-lined spectrum of hydrogen. At higher temperatures neither the new curve nor those of Reiche agree completely with the experimental points.

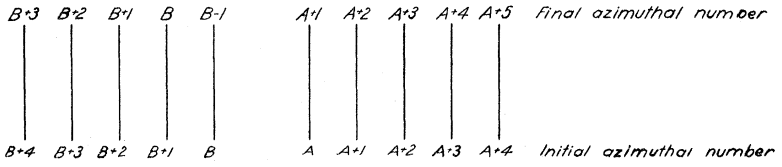

Fig. 1

It has seemed worth while to present the results of the calculations since half quantum numbers have recently shown a surprising tendency to appear, and have already been considered by Kratzer[4] as a definite possibility in attempting to account for band spectra. It is believed that the results are sufficient to show that half quantum numbers must also be regarded as a definite possibility in attempting a theory of rotational specific heats.

Rotational Quantum Numbers and Infra-Red Spectra

Information as to the possible states of rotation of a diatomic molecule can best be obtained from a consideration of the rotation-oscillation spectra of the hydrogen-halides. These spectra consist of approximately equally spaced lines with the omission of one line in the center as shown diagrammatically in Fig. 1.

[1] Eucken, Sitzungsber d. Preuss. Akad. d. Wiss. 1912, p. 148
[2] Scheel and Heuse, Ibid. 1913, p. 44; Ann. der Phys. **40**, 473 (1913)
[3] Reiche, Ann. der Phys. **58**, 657 (1919)
[4] Kratzer, Ergebnisse der Exakten Naturwissenschaften **1**, 332, 1922

Except for a possible uncertainty as to the correct way of assigning rotational quantum numbers to the different lines, the theory of such spectra has been presented by Kratzer[5] in a very satisfactory form, which not only takes account of the rotation of the molecules about their center of gravity and the oscillation of the atoms along their connecting line but also allows for the mutual interaction of rotation and oscillation and for the possibility that the law of force between the atoms may be such as to lead to non-harmonic oscillation.

For our immediate purpose we shall not need the complete theory but may consider that the energy taken up by the molecule accompanying an *absorption* line in the fundamental series is given by the approximate equation

$$h\nu = h\nu_0 + (m'^2 - m^2)h^2/8\pi^2 J \tag{1}$$

where ν is the frequency of the line, ν_0 the frequency of the oscillation, m and m' the azimuthal quantum numbers before and after absorption, and J the moment of inertia of the molecule. Using the Bohr selection principle to restrict the change in azimuthal quantum number to the values

$$m' = m \pm 1 \tag{2}$$

it can easily be shown that Eq. (1) does lead to a set of equally spaced lines, the *absorption* lines of higher frequency (to the right of the gap), being associated with unit increase in azimuthal quantum number and the lines to the left of the gap being associated with unit decrease in azimuthal quantum number, and furthermore the initial azimuthal quantum number of the molecule before absorption increasing by unity for each successive line counted from the center outwards.

We may use the above results to assist us in determining the possible absolute values for the initial quantum numbers. Referring again to Fig. 1, let the initial quantum numbers for the lines to the right of the gap be A, $A+1$, $A+2$, . . . and for those to the left of the gap to be B, $B+1$, $B+2$, ... where A and B are the two unknown quantities concerning which information is desired.

Since the interval between the lines with initial quantum numbers B and A is twice that between the lines A and $A+1$, it is evident from Eq. (1) that we may write the equation

$$[(A+1)^2 - A^2] - [(B-1)^2 - B^2] = 2[(A+2)^2 - (A+1)^2] - 2[(A+1)^2 - A^2]$$

which reduces to

$$B + A = 2 \tag{3}$$

Furthermore, since we accept the hypothesis that quantum numbers

[5] Kratzer, Zeitschr. f. Phys. **3**, 289 (1920)

can only differ by an integer, we may write for the difference between B and A, the equation

$$B-A=i, \text{ where } i=0, \pm 1, \pm 2, \text{ etc} \tag{4}$$

Let us now examine the different possible cases that can be obtained by taking different values for i.

Case I. $i=0; A=B=1$.

This is the assumption originally made by Kratzer.[5] It makes the lowest possible quantum number unity for a non-oscillating molecule and, since $B-1$ occurs after absorption, zero for an oscillating molecule, and thus has the disadvantage of allowing zero rotation in one case but not in the other.

Case II. $i=1; A=\frac{1}{2}; B=3/2$.

This is the case we shall test in this paper. It makes the lowest possible azimuthal quantum number one half, the same for oscillating and non-oscillating molecules.

Case III. $i=2; A=0; B=2$.

This case would allow zero rotation for the non-oscillating molecule but not for the oscillating molecule, which is inherently improbable and has been shown by Reiche to lead to impossible specific heat curves.

It can easily be seen that cases where i is assumed negative or numerically greater than two are not feasible.

Quantization in Space for Half Quantum Numbers

If now we proceed on the new basis that the azimuthal quantum numbers can take the values $\frac{1}{2}$, $3/2$, $5/2$, . . . , or in general $n-\frac{1}{2}$, where $n=1, 2, 3$ . . . we may develop an elementary theory of quantization in space. If we assume in agreement with the work of Epstein[6] that the angular momentum of the molecule associated with the azimuthal quantum number, and the component of this angular momentum in the "specified" direction, can both be quantized, we may write for the azimuthal angular momentum,

$$p=(n-\tfrac{1}{2})h/2\pi \tag{5}$$

and for the component momentum in the "specified" direction

$$p_\psi=(n_1-\tfrac{1}{2})h/2\pi \tag{6}$$

where $(n-\frac{1}{2})$ is the azimuthal quantum number and $(n_1-\frac{1}{2})$ is the equatorial quantum number. The necessity of using half equatorial quantum numbers as well as half azimuthal quantum numbers arises from our acceptance of the hypothesis that quantum numbers can differ only by an integer combined with the hypothesis that the lowest

[6] Epstein, Ber. d. Phys. Ges. **19**, 116 (1917)

possible values for equatorial and azimuthal quantum numbers are the same.[7]

If α is the angle between the total angular momentum and the "specified" direction we may evidently write

$$\cos\alpha=\frac{p_\psi}{p}=\frac{n_1-\frac{1}{2}}{n-\frac{1}{2}}=\frac{2n_1-1}{2n-1} \tag{7}$$

Since n and n_1 must be integers greater than zero and $\cos\alpha$ must be less than unity, Eq. (7) imposes definite restrictions on the possible values of α. Giving n the successive value 1, 2, 3, . . . we can easily determine the possible values of α which are summarized in the following table.

		Number of values of α
Case I	$n=1$; $n_1=1$; $\cos\alpha=1$	1
Case II	$n=2$; $n_1=1$; $\cos\alpha=1/3$	2
	$n_1=2$; $\cos\alpha=1$	
Case III	$n=3$; $n_1=1$; $\cos\alpha=1/5$	3
	$n_1=2$; $\cos\alpha=3/5$	
	$n_1=3$; $\cos\alpha=1$	
Case IV	$n=4$; $n_1=1$; $\cos\alpha=1/7$	4
	$n_1=2$; $\cos\alpha=3/7$	
	$n_1=3$; $\cos\alpha=5/7$	
	$n_1=4$; $\cos\alpha=1$	

etc.

If we count positive and negative rotations separately, as is apparently required by the Bohr correspondence principle,[8] we may then write

$$p_n=2n \tag{8}$$

for the a priori probability of a state having the azimuthal quantum number

$$m=(n-\tfrac{1}{2}) \tag{9}$$

In connection with the above discussion of a priori probabilities, it should be noted how simply we have arrived at the conclusion that the a priori probabilities of the successive energy levels stand in the ratio 1, 2, 3, etc., without resorting to any artificial rejection of the states of no rotation or states where the plane of rotation is parallel to the specified direction.

[7] Compare Landé, Zeitschr. f. Phys. **11**, 357 (1922)

[8] Bohr, "On the Quantum Theory of Line-Spectra," Copenhagen Academy 1918, Part I, p. 25.

General Equation for Rotational Specific Heat

We may evidently write for the rotational heat capacity of one mol of an ideal diatomic gas consisting of molecules of the rigid "dumb-bell" model, the expression

$$C_R = N\frac{d}{dT}\left[\frac{\Sigma p_m e^{-m^2\sigma} m^2 kT\sigma}{\Sigma p_m e^{-m^2\sigma}}\right] \tag{10}$$

where, following Reiche[3] we have put

$$\sigma \equiv h^2/8\pi^2 JkT \tag{11}$$

and where N is the number of molecules in a gram-molecule, m is the azimuthal quantum number, J is the moment of inertia of the molecule, p_m is the a priori probability corresponding to m, and the summations are to be taken for all possible values of the azimuthal quantum number.

If now, following the procedure of Reiche[3] we write

$$Q = \Sigma p_m e^{-m^2\sigma} \tag{12}$$

it can readily be shown that Eq. (10) can be rewritten in the form

$$\frac{C_R}{R} = \sigma^2 \frac{d^2 \log Q}{d\sigma^2} \tag{13}$$

Using the a priori probabilities given by Eq. (8), corresponding to the quantum numbers given by (9) we may rewrite (12) for our case in the form

$$Q = \Sigma_1^\infty 2n e^{-(n-\frac{1}{2})^2\sigma} \tag{14}$$

Approximations for High, Low, and Intermediate Temperatures

At very *high* temperatures where σ is small we may evidently write the approximations

$$\begin{aligned} Q &= \int_0^\infty 2n e^{-(n-\frac{1}{2})^2\sigma} dn = \frac{1}{\sigma}[1+\tfrac{1}{2}\sqrt{(\pi\sigma)}]; \\ \log Q &= -\log\sigma + \tfrac{1}{2}\sqrt{(\pi\sigma)}; \\ C_R/R &= 1 - \sqrt{(\pi\sigma)}/8 \end{aligned} \tag{15}$$

and note that the value of C_R/R approaches unity as the temperature rises.

At very low temperatures where σ is large we may evidently write the approximations

$$\begin{aligned} Q &= 2e^{-\sigma/4}(1+2e^{-2\sigma}) \\ \log Q &= \log 2 - \tfrac{1}{4}\sigma + 2e^{-2\sigma} \\ C_R/R &= 8\sigma^2 e^{-2\sigma} \end{aligned} \tag{16}$$

At *intermediate* temperatures, we can generally obtain sufficient accuracy by considering the first four terms in Q. Eq. (13) can then be written

$$\frac{C_R}{R}=\sigma^2\frac{(1/16)e^{-\sigma/4}+(81/8)e^{-9\sigma/4}+(1875/16)e^{-25\sigma/4}+(2401/4)e^{-49\sigma/4}}{e^{-\sigma/4}+2e^{-9\sigma/4}+3e^{-25\sigma/4}+4e^{-49\sigma/4}} - \sigma^2\frac{(1/4)e^{-\sigma/4}+(9/2)e^{-9\sigma/4}+(75/4)e^{-25\sigma/4}+49e^{-49\sigma/4}}{e^{-\sigma/4}+2e^{-9\sigma/4}+3e^{-25\sigma/4}+4e^{-49\sigma/4}} \tag{17}$$

The Specific Heat Curve for Hydrogen

Making use of Eqs. (16) and (17) a number of values for C_R/R have been calculated for different values of σ, and are tabulated below. The temperatures in the third column are related to the values of σ by the equation

$$T=286/\sigma \tag{18}$$

This corresponds to a value for the moment of inertia of the hydrogen molecule.

$$J=1.387\times10^{-41}\text{gm cm}^2 \tag{19}$$

and gives the best correspondence between the experimental data and the calculated curve.

Table I

σ	$1/\sigma$	T	C_R/R
7	0.1429	40.9	0.000
6	0.1667	47.7	0.003
5	0.2	57.2	0.008
4	0.25	71.5	0.042
3 1/5	0.3125	89.4	0.151
2 2/3	0.375	107.3	0.270
2	0.5	143.0	0.533
1 3/5	0.625	178.8	0.729
1 1/3	0.75	214.5	0.813
1	1	286.0	0.845
4/5	1.25	357.7	0.852

Comparison with the Experimental Data and with the Curves of Reiche

The agreement between the calculated curve and the experimental values of Eucken and of Scheel and Heuse as cited by Reiche[3] is shown in Fig. 2. The full line is the best smooth curve through the calculated points, and the experimental points are indicated by crosses. The dotted lines give the upper portions of Reiche's curves Nos. III, IV and V. At low temperatures these curves of Reiche are in as satisfactory agreement as our own with the experimental points. At the higher temperatures none of the curves agree with all the experimental points.

Reiche's calculations employing different assumptions as to the form of Q may now be compared with the calculations made in this paper.

(I) $$Q=\Sigma_0^{\infty}(2m+1)e^{-m^2\sigma}.$$

This form for Q is obtained on the assumption that the lowest possible azimuthal quantum number is zero, and that positive and negative rotations are to be counted twice in determining a priori probabilities. It leads to a specific heat curve with a maximum value for C_R/R at low temperatures and cannot agree with the experimental facts.

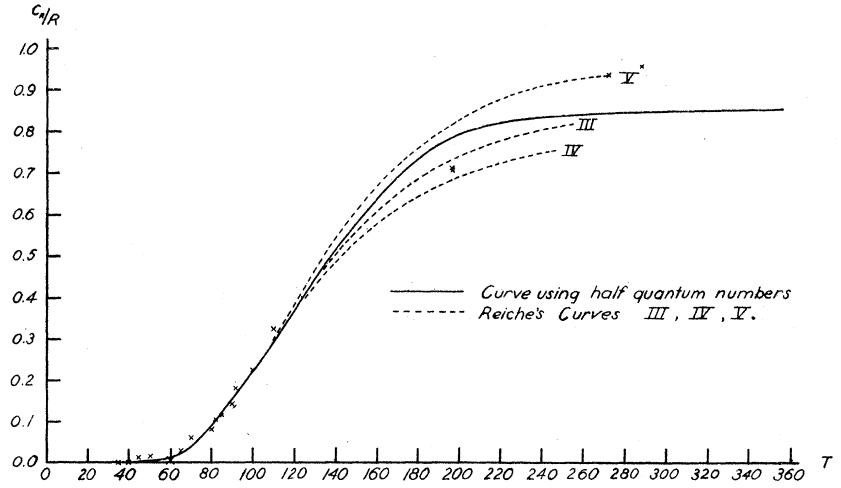

Fig. 2

(II) $$Q=\Sigma_0^{\infty}(m+1)e^{-m^2\sigma}$$

This form for Q is obtained on the same assumptions as above except that positive and negative rotations are only counted once in determining a priori probabilities, a procedure, however, which is apparently not in agreement with the correspondence principle. It also leads to an impossible specific heat curve with a maximum value for C_R/R at low temperatures.

(III) $$Q=\Sigma_1^{\infty}(2m+1)e^{-m^2\sigma}.$$

This form for Q is obtained by counting positive and negative rotations twice, but excluding the possibility of no rotation. With the value for the moment of inertia $J=2.214\text{x}10^{-41}$ it agrees with the experimental points at low temperatures but fails at high temperatures.

(IV) $$Q=\Sigma_1^{\infty}(m+1)e^{-m^2\sigma}.$$

This form for Q is obtained on the same assumptions as for (III) but counting positive and negative rotations only once. With the value for the moment of inertia $J=2.293\text{x}10^{-41}$, it agrees with the experimental points at low temperatures but fails at high temperatures.

(V) $$Q=\Sigma_1^{\infty}2me^{-m^2\sigma}.$$

This form for Q is obtained on the same assumption as for (I) but ex-

cludes not only the case of no rotation but somewhat arbitrarily all cases where the plane of rotation is parallel to the specified direction. With the value $J=2.095\times10^{-41}$ it agrees with experimental points at low temperatures and with the two points at the highest temperatures but fails to agree with the points at 197°.

(VI) $$Q=\Sigma_0^\infty(2n+1)e^{-(n^2+n+\frac{1}{2})\sigma}.$$

This form for Q is based on calculations made by Planck, using the second form of quantum theory. It leads to a specific heat curve with a maximum 10 per cent greater than the classical value and cannot agree with the experimental facts.

(VII) $$Q=\Sigma_1^\infty 2ne^{-(n-\frac{1}{2})^2\sigma}.$$

This is the form for Q discussed in this paper. It takes the lowest possible azimuthal quantum number as one half and makes no arbitrary exclusions in determining the a priori probabilities. With the value for the moment of inertia $J=1.387\times10^{-41}$ it agrees with the experimental data at low temperatures as well as any curve of Reiche's. This lower value for the moment of inertia is of interest since Sommerfeld[9] concludes from the many lined spectrum of hydrogen that the moment of inertia of an excited hydrogen molecule is 1.9×10^{-41}, and the moment of inertia of the unexcited molecules involved in determining specific heats at low temperatures must be lower than that figure, a condition which is met by the new curve and not by those of Reiche. The failure of all the curves at the higher temperatures may be due to the over simplification involved in assuming the rigid "dumb-bell" model for the hydrogen molecule, which can at best be regarded only as a first approximation.[10]

The assumption of half quantum numbers has also been used for calculating the entropies of diatomic gases and shown to agree as well with the experimental facts as any of the older assumptions.[11]

In conclusion the writer wishes to express his appreciation to Professors Charles G. Darwin and Paul S. Epstein for very helpful suggestions and criticisms.

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May 16, 1923.

[9] Sommerfeld, "Atombau und Spektrallinien," 3rd edition, page 535, Braunschweig 1922. It should be noted that the change to half quantum numbers does not affect the relation $\Delta\nu=h/4\pi^2J$ for the spacing between lines.

[10] At high enough temperatures, an appreciable amount of energy of oscillation may enter in. See the treatment of Kemble and Van Vleck, Phys. Rev. **21**, 653, 1923, which has appeared since the above was written.

[11] See Tolman and Badger, J. Amer. Chem. Soc. **45**, 2277, 1923.